Structural Interconversions of Dichlorobis(triphenylphosphine)-nickel(II) in Various Solvents

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(Received November 15, 1978)

Structural interconversions, ligand exchange, the temperature- and concentration-dependent equilibrium of configurational isomers, and the solvolysis of $NiCl_2(Ph_3P)_2$ in various solvents have been studied. The MCD and absorption spectra were employed, together with the calculation based on ligand-field theory and the NMR spectra. Paramagnetic tetrahedral $NiCl_2(Ph_3P)_2$ and the solvated paramagnetic octahedral $NiCl_2(Ph_3P)_2(dmso)_2$ are in equilibrium in the coordinating solvent DMSO. The ratio of the former to the latter increases with the rise of concentration and temperature. Configurational isomers of $NiCl_2(Ph_3P)_2$, a paramagnetic tetrahedral one and a diamagnetic square-planar one, are found in a non-coordinating solvent $CHCl_3$. The former species decreases gradually and a yellow precipitate is formed. The same two species, and two other solvated paramagnetic tetrahedral and octahedral species, $NiCl_2(CH_3CN)_2$ and $NiCl_2(CH_3CN)_4$, are found to be in equilibrium in CH_3CN.

Dihalogenonickel(II) tertiary phosphine complexes have been used as a catalyst for a number of synthetic reactions. The solvent and the temperature are often important factors for the catalytic activity. A number of studies[1-5] have been reported on the dynamic interconversion between the paramagnetic tetrahedral form and the diamagnetic square-planar form of these complexes in non-coordinative solvents. By measuring the absorption spectra and the magnetic susceptibility of $NiCl_2(Ph_3P)_2$ in a solution of inert solvents (for example, $CHCl_3$ and benzene), it has been shown that there is a small amount of the trans-square-planar diamagnetic species in equilibrium with the tetrahedral paramagnetic species.[2,3] However, few investigations on the molecular conformation and the dynamic behavior in coordinative solvents are reported.

The molecular structure of $NiCl_2(Ph_3P)_2$ in crystal form is known[6] to be: Ni–Cl=2.27 Å, Ni–P=2.28 Å, ∠Cl–Ni–Cl=123°, ∠P–Ni–P=117°. Its polarized single-crystal electronic spectrum was assigned by taking the effective site-symmetry as C_{2v}.[7] When the molecule is dissolved in various solvents, it may take a tetrahedral, a square-planar, or an octahedral form, and will show a characteristic electronic spectrum depending on each configuration. In addition, the magnetic circular dichroism (MCD) spectrum has the sign as well as the magnitude characteristic of each electronic transition,[8,9] and can be a very powerful means for clarifying the complexity of the absorption spectra, providing further information with which to understand the molecular state.

The absorption and MCD spectra indicate simply the sum of spectra arising from each species in the equilibrium mixture. On the other hand, NMR spectra can be used in another way: if the frequency separation between resonance lines of species in equilibrium is smaller than the frequency of the interconversion or the ligand exchange, only a single line at the average frequency is observed. NMR spectra will thus provide the evidence for the degree of molecular lability and the rate of ligand exchange.

We have therefore studied the structural interconversions of $NiCl_2(Ph_3P)_2$ in various solvents, such as dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), acetonitrile (CH_3CN), *etc.*, by the MCD and absorption spectra, the calculations based on ligand-field theory, and the NMR spectra.

Experimental

The following compounds used in this study were prepared and recrystallized according to previously reported procedures; $NiCl_2(Ph_3P)_2$,[1] $Ni(SCN)_2(Ph_3P)_2$,[1] $(Et_4N)_2NiCl_4$,[10] $[Ni(dmf)_6](ClO_4)_2$,[11] $[Ni(dmso)_6](ClO_4)_2$.[12] All solvents were obtained commercially (Guaranteed Reagent of Nakarai Chemical Co.). Acetonitrile was dried and purified by fractional distillation with anhydrous calcium chloride.

Absorption spectra in the range 10000 to 13000 cm^{-1} were measured by a JASCO J-40 spectrophotometer, to which an electro-magnet of field strength 8.9 kG is attached. The spectra in the other ranges were measured with the apparatus previously described.[13,14] NMR spectra were obtained by using a JEOL JNM-PS-100 instrument equipped with a variable-temperature probe. All of the spectra were measured just after preparing the solution, unless otherwise specified.

Results and Discussion

MCD and Absorption Spectra. The MCD spectra of the charge-transfer bands in tetrachloro nickel(II) ions have been studied,[15] but the MCD spectra of the d-d transitions have not yet been reported. The spectrum in solution shows a great change depending on the solvent. The MCD and the absorption spectra of a solution of $(Et_4N)_2NiCl_4$ in CH_3CN are shown in Fig. 1. The absorption spectrum is very similar to the spectrum of Ni(II) ion in tetrahedral sites in the crystal of Cs_2ZnCl_4,[16] and it does not show any significant change when the excess tetramethylammonium chloride (Et_4NCl) is added to the solution. Therefore we may consider that the spectrum arises from a tetrahedral $NiCl_4^{2-}$ ion. The absorption band in the range 13000—17000 cm^{-1} has been assigned as a transition $^3T_1(F)\rightarrow{}^3T_1(P)$.[17] The MCD spectrum in this absorption region shows a dispersion with positive sign in the lower energy region and negative sign in the higher energy region (let us call this "*positive dispersion*").

The MCD spectra of d-d transitions in some octahedral nickel(II) complexes have been studied extensively.[18,19] In octahedral nickel(II) complexes, there are three spin-allowed d-d transitions: $^3A_2\rightarrow{}^3T_2$, $^3T_1(F)$,

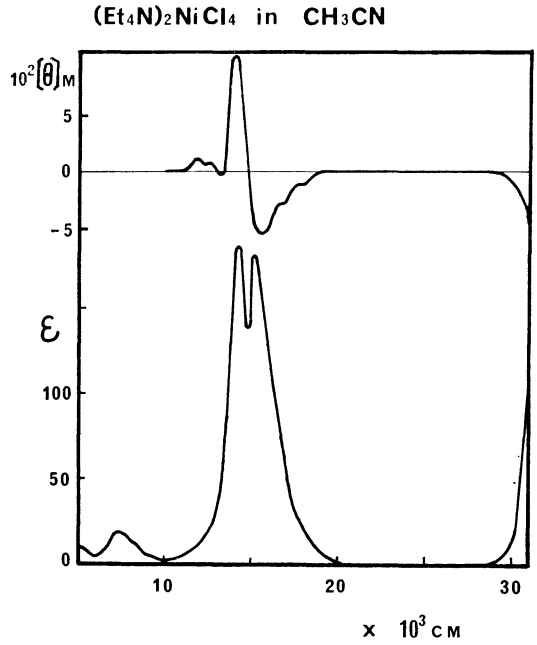

Fig. 1. MCD and absorption spectra of $(Et_4N)_2NiCl_4$ in CH_3CN at room tempepature. $[\theta]_M$ is the molar ellipticity per unit magnetic field. ε is molar extinction coefficient.

and $^3T_1(P)$, in the region from near-infrared to visible. The molar extinction coefficients of these d-d transitions are smaller than those in the tetrahedral complexes, because in the latter complexes there is no center of inversion symmetry and there is greater d-p mixing. The MCD and absorption spectra of a solution of $[Ni(dmf)_6](ClO_4)_2$ in DMF and a solution of $[Ni(dmso)_6](ClO_4)_2$ in DMSO are shown in Figs. 2 and 3 respectively. The MCD spectrum of the band in the 12000—16000 cm^{-1} region is mainly negative and shows a small positive value in the higher energy region (let us call this "*negative dispersion*"). The sign of the dispersion is opposite to that of the tetrahedral complex observed in the 13000—17000 cm^{-1} region. This characteristic difference is very useful in distinguishing whether the complex in solution is in octahedral or in tetrahedral symmetry.

The compounds NiX_2L_2 (L=tertiary phosphines, X=Cl, Br, I, and SCN) have been studied in a series of papers.[1-3] Some of them were found to be in equilibrium of the paramagentic tetrahedral form and the diamagnetic square-planar form in inert solvents. The thiocyanato-complex, $Ni(SCN)_2(Ph_3P)_2$, has been found to be diamagnetic and trans-square planar.[3] The MCD and absorption spectra are shown in Fig. 4. The absorption spectrum shows bands only at energy regions higher than 15000 cm^{-1} and the high-intensity absorption bands at about 24000 and 31000 cm^{-1} are generally referred to as charge-transfer bands. The magnitude of the MCD in comparison with that of the absorption, which may be indicated by the magnitude of $[\theta]_M/\varepsilon$, in the diamagnetic square planar nickel(II) complex is less than 10% of those found in the paramagnetic tetrahedral and the paramagnetic octahedral nickel(II) complexes. This characteristic difference can be useful in finding whether the complex in solution is paramagnetic or diamagnetic.

The MCD and absorption spectra of dichlorobis(triphenylphosphine)nickel(II), $NiCl_2(Ph_3P)_2$, were found to change greatly depending on the solvent, the concentration of the solution, and the temperature. The dependence on the concentration in DMSO is shown in Fig. 3. It shows a drastic change in a narrow range of the concentration. The spectrum of 0.25 M solution shows a strong absorption band in the range 14000—18000 cm^{-1}, and the MCD of the band shows a positive dispersion, which is characteristic of the paramagnetic tetrahedral species. However, as the concentration is reduced to 0.05 M, the intensity of the band in this range decreases and the intensities of the bands at about 7500, 12500, and 23000 cm^{-1} increase. This fact indicates that the paramagnetic tetrahedral species and the paramagnetic octahedral

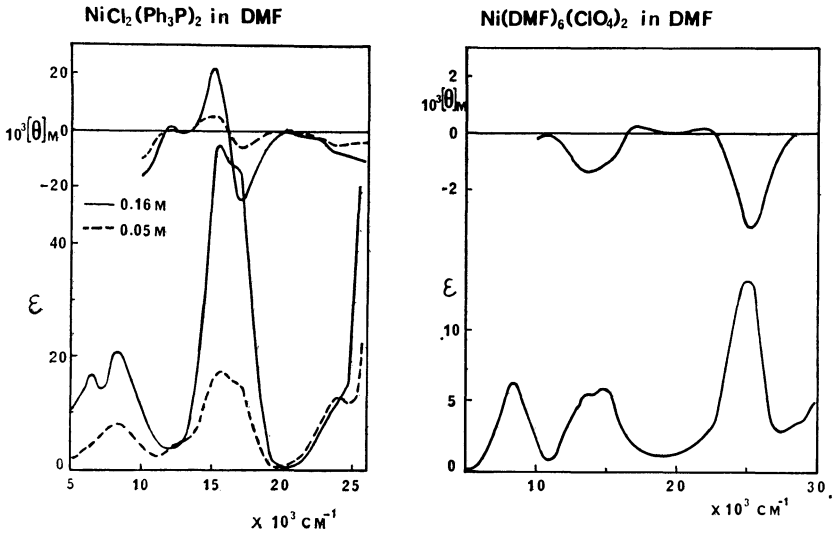

Fig. 2. MCD and absorption spectra of $Ni(dmf)_6(ClO_4)_2$ and the concentration dependence of the spectra of $NiCl_2(Ph_3P)_2$ in DMF at room temperature.

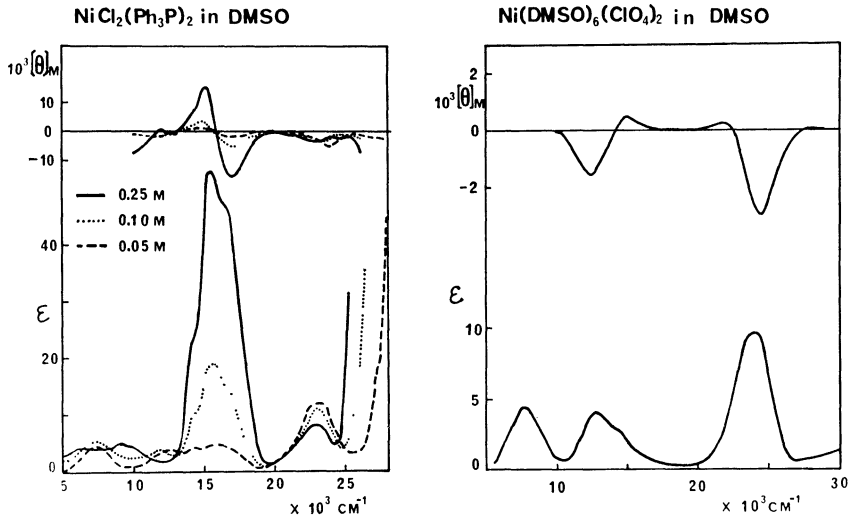

Fig. 3. MCD and absorption spectra of $Ni(dmso)_6(ClO_4)_2$ and the concentration dependence of the spectra of $NiCl_2(Ph_3P)_2$ in DMSO at room temperature.

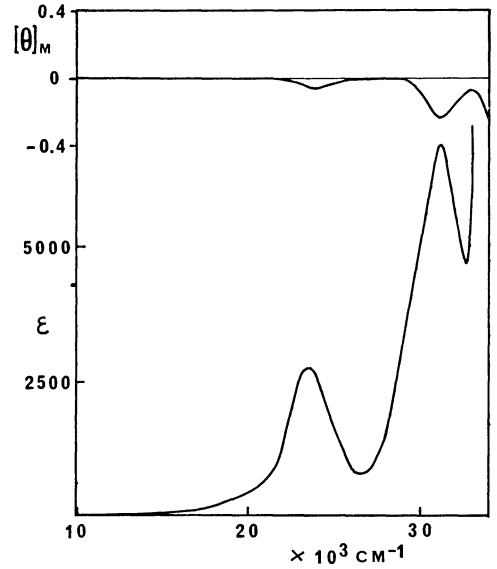

Fig. 4. MCD and absorption spectra of 0.02 M solution of $Ni(SCN)_2(Ph_3P)_2$ in benzene at room temperature.

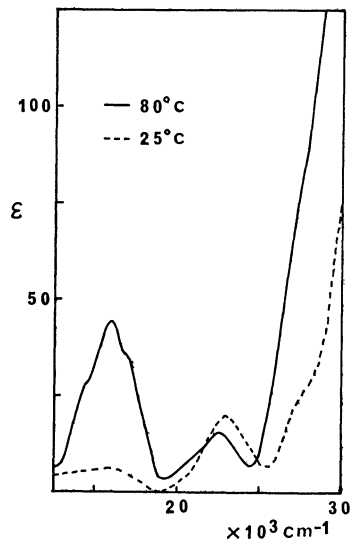

Fig. 5. Temperature dependence of the absorption spectrum of 0.05 M solution of $NiCl_2(Ph_3P)_2$ in DMSO.

species are in equilibrium in the solution and the ratio of the former to the latter decreases as the concentration decreases.

When the temperature of the 0.05 M solution is raised (see Fig. 5), the absorption spectrum becomes very similar to the one observed in the solution of higher concentration at room temperature. When this solution is cooled to room temperature again, the spectrum returns to the one measured before heating. This fact indicates that the octahedral complex in 0.05 M solution at room temperature is $NiCl_2(Ph_3P)_2(dmso)_2$, and as the temperature is raised it tends to become tetrahedral $NiCl_2(Ph_3P)_2$ by expelling the coordinated solvent molecules.

The spectrum is found to change slowly in the course of time (see Fig. 6), and the crystal of triphenylphosphine (Ph_3P) is found to grow in a couple of days after preparing the solution. The spectrum, which is measured after several days, is identified to that of a paramagnetic octahedral species, but it is not identical with the spectrum of $Ni(dmso)_6^{2+}$. It appears therefore that the coordinated Ph_3P tends to be removed gradually and thus the solvated compound $NiCl_2(dmso)_4$ is produced.

In 0.25 M solution, the intensities of absorption bands due to the terahedral species are much greater than those due to the octahedral species. However the molar concentrations of the tetrahedral species and the octahedral species would be almost the same, since the molar extinction coefficients of the bands due to the tetrahedral species are much greater than those due to the octahedral ones.

The spectral behavior observed in DMF solution is similar to that observed in DMSO solution. If we compare the spectrum of 0.05 M $NiCl_2(Ph_3P)_2$ solution in DMF with that in DMSO at room temperature

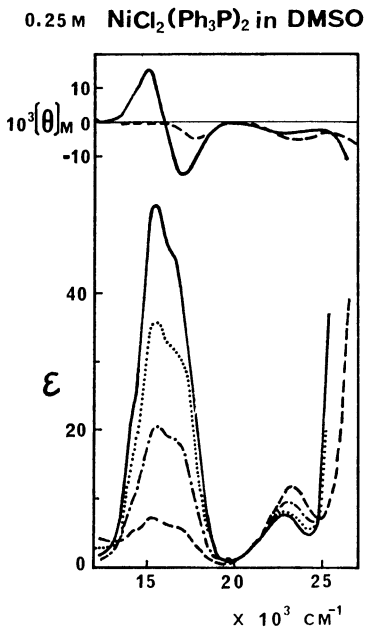

Fig. 6. Change of MCD and absorption spectra of 0.25 M $NiCl_2(Ph_3P)_2$ solution in DMSO at room temperature as a function of time. Measured immediately after preparing the solution (——), after 24 h (----), after 72 h (·—·—), after one week (— —). The sample was kept in dark place at 25 °C.

(Figs. 2 and 3), it is understood that the tetrahedral form of $NiCl_2(Ph_3P)_2$ is slightly more stable in DMF than in DMSO.

The spectrum of $NiCl_2(Ph_3P)_2$ in CH_3CN (Fig. 7) shows that the paramagnetic tetrahedral form of this complex is more stable in CH_3CN than in DMSO or in DMF. The absorption band in the range 14000—18000 cm^{-1} is assigned as a transition $^3T_1(F) \rightarrow {}^3T_1(P)$ of a tetrahedral species, because of the magnitude of the extinction coefficient and because of the MCD spectrum, whose sign and magnitude are very similar to those of $NiCl_4^{2-}$ ion (see Fig. 1). The extinction coefficient of this band in 0.01 M solution is as large as those observed in the more concentrated solutions in DMSO and in DMF (0.25 M in the former and 0.16 M in the latter. See Figs. 2 and 3). If the observed absorption bands were due to a fairly large amount of octahedral species, the apparent molar extinction coefficient should be much smaller. Therefore the complex will be mostly tetrahedral in 0.01 M solution in CH_3CN.

The extinction coefficient of the shoulder-like absorption band at about 24000 cm^{-1} in Fig. 7 is greater than that of the transition $^3A_2 \rightarrow {}^3T_1(P)$ of an octahedral species. The ratio $[\theta]_M/\varepsilon$ is smaller than that of the paramagnetic species, and it is close to the value of $[\theta]_M/\varepsilon$ observed in $Ni(SCN)_2(Ph_3P)_2$ solution in benzene (see Fig. 4), the complex in the solution is known to be diamagnetic square plane.[3] Since the molar extinction coefficient of the diamagnetic species is much greater than that of the paramagnetic species, even a small amount of diamagnetic species causes a strong absorption. Thus the band at about 24000 cm^{-1} may be identified as the absorption due to a small amount of diamagnetic square-plane species in CH_3CN solution.

Absorption bands in the energy region higher than about 27000 cm^{-1} will be mainly attributed to the charge transfer bands of the paramagnetic tetrahedral species, since the sign and magnitude of the MCD and the ratio $[\theta]_M/\varepsilon$ are in good agreement with those observed in charge transfer bands of tetrahalogenonickel(II) complexes.[15]

The spectra of $NiCl_2(Ph_3P)_2$ in non-coordinating solvents, such as chloroform, dichloromethane, and benzene, are different from those in coordinating solvents. The spectrum of 0.05 M solution in $CHCl_3$ is shown in Fig. 8. The absorption spectrum in the

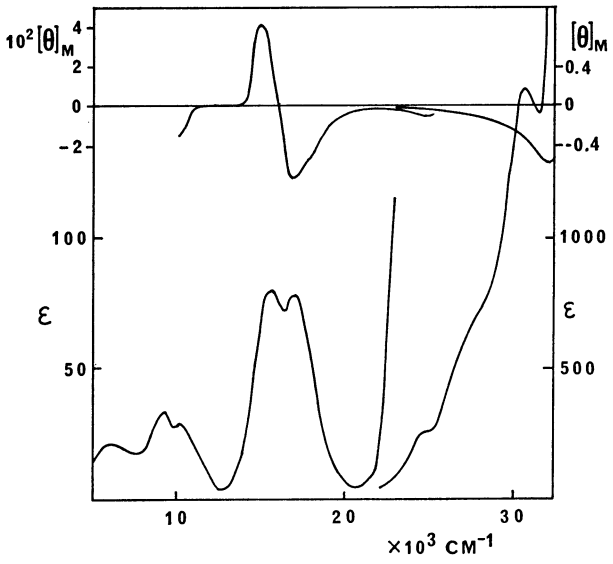

Fig. 7. MCD and absorption spectra of 0.01 M solution of $NiCl_2(Ph_3P)_2$ in CH_3CN at room temperature.

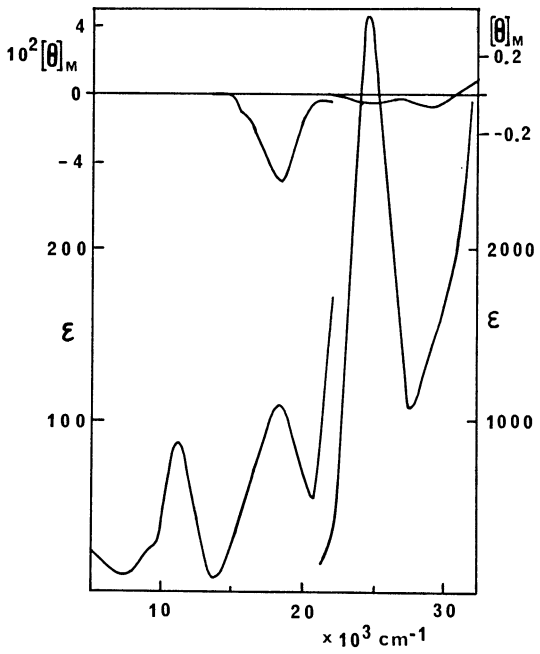

Fig. 8. MCD and absorption spectra of 0.05 M solution of $NiCl_2(Ph_3P)_2$ in $CHCl_3$ at room temperature.

range 5000—20000 cm^{-1} is similar to the crystal absorption spectra of $NiCl_2(Ph_3P)_2$, in which the nickel(II) ion is reported to be in "effective" C_{2v} point-group symmetry.[7] This presumably means that the molecule, which shows a similar absorption spectrum to that in crystal, retains the distorted tetrahedral configulation in non-coordinating solvents. It should be noted that the MCD spectrum of the band in the region of 15000—20000 cm^{-1} is simply negative and that it is different from those observed in coordinating solvents.

The absorption bands in the energy region higher than 22000 cm^{-1} will be of the diamagnetic square-plane species, since the ratios $[\theta]_M/\varepsilon$ of the bands are very close to the one observed in $Ni(SCN)_2(Ph_3P)_2$ solution in benzene. The high extinction coefficient and the small value of $[\theta]_M/\varepsilon$ for the absorption band at about 25000 cm^{-1} are characteristic of diamagnetic square-plane nickel(II) complexes. The intensity of the band is stronger in $CHCl_3$ than in CH_3CN. It appears therefore that the proportion of the diamagnetic species is greater in $CHCl_3$ than in CH_3CN.

Calculations Based on Ligand-field Theory. Energy levels of $NiCl_2(Ph_3P)_2$ and $NiCl_2(Ph_3P)_2(dmso)_2$ are calculated by the following approximation. The magnitude of ligand field parameters D_q of $NiCl_4^{2-}$, $Ni(Ph_3P)_4^{2+}$ in T_d symmetry and $Ni(dmso)_6^{2+}$ in O_h symmetry are estimated to be 350, 550, and 850 cm^{-1} respectively. The ligands, Cl, Ph_3P, and DMSO, are approximated by point charges and the magnitudes of the point charges $-Ze$ are evaluated by using the relation: $D_q=2Ze^2\langle r^4\rangle/27a^5$ in T_d symmetry and $D_q=Ze^2\langle r^4\rangle/6a^5$ in O_h symmetry, where $-Ze$ is the point charge and a is the distance between the nickel atom and the point charge. From the data of X-ray analysis,[17] we assumed the distances between the point charges and nickel atom to be Ni–Cl=2.27 Å and Ni–P=2.28 Å in tetrahedral form, and Ni–Cl=2.38 Å, Ni–P=2.39 Å, and Ni–O=2.10 Å in octahedral form. The values of $\langle r^2\rangle$ and $\langle r^4\rangle$ were calculated by using an analytical SCF function for nickel atoms obtained by Clementi:[20] $\langle r^4\rangle_{Ni(3d)}=3.997a_0^4$ and $\langle r^2\rangle_{Ni(3d)}=1.220a_0^2$, where a_0 is the Bohr radius. The point charges of $NiCl_2(Ph_3P)_2$ are put in the direction of the regular tetrahedron. This may not be an accurate structure since the crystal-structure determination shows that the Cl–Ni–Cl and P–Ni–P bond angles are 123° and 117°, respectively, which are greater than the tetrahedral 109°28′. The effect of lower symmetry C_{2v} is reflected in the magnitude of point charges and distances from the metal. The point charges of $NiCl_2(Ph_3P)_2(dmso)_2$ are put in the direction of regular octahedron so that the same ligands are in trans positions. All the possible configurations of d^8 electrons are considered, and the effect of the spin-orbit interaction is included completely. The spin-orbit coupling constant ζ is assumed to be that of free nickel(II) ion: $\zeta=649$ cm^{-1}. The results of energy level calculations are shown schematically in Figs. 9 and 10.

The energy levels of $NiCl_2(Ph_3P)_2(dmso)_2$ are similar to those of $Ni(dmso)_6^{2+}$. The MCD of the paramagnetic octahedral nickel(II) complexes has been found to arise from the MCD C-term,[18,19] which originates in

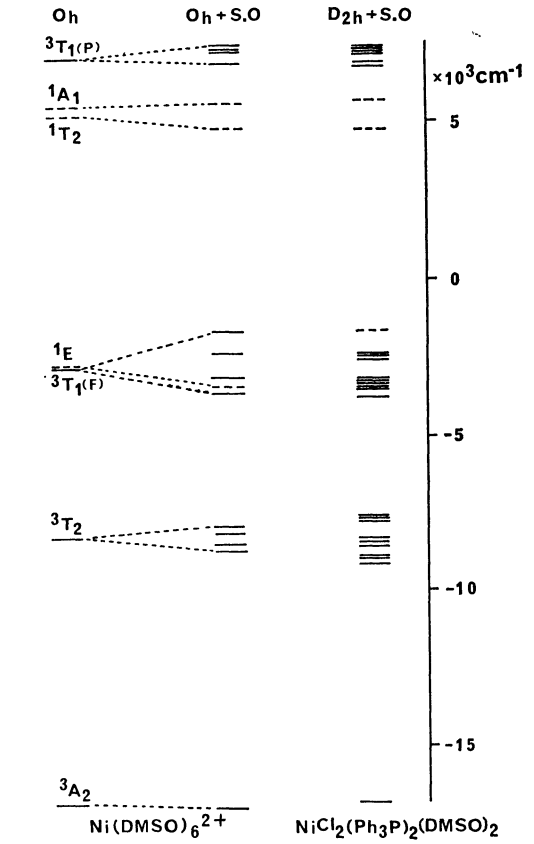

Fig. 9. Calculated energy levels of $Ni(dmso)_6^{2+}$ and $NiCl_2(Ph_3P)_2(dmso)_2$.

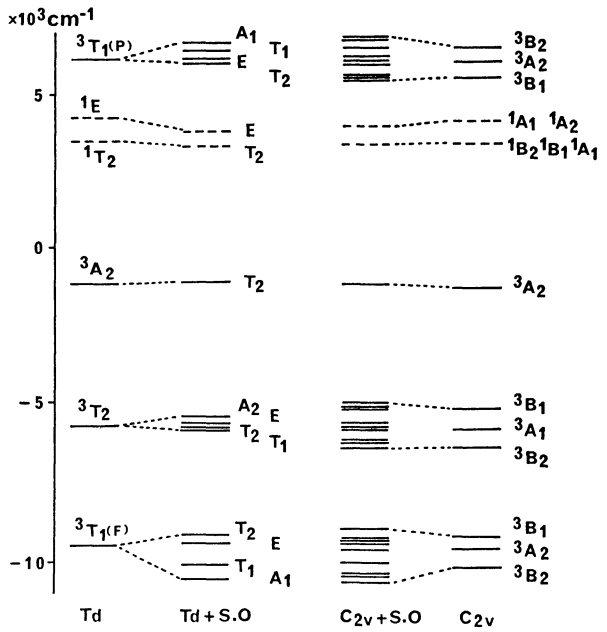

Fig. 10. Calculated energy levels of $NiCl_2(Ph_3P)_2$. The energy levels in rigorously tetrahedral field and in the lower symmetry field are denoted as T_d and C_{2v}, respectively. The inclusion of spin-orbit coupling is shown by adding +S.O.

the population difference among the levels of the ground state $^3A_2$ split by the Zeeman effect. Since the ground state of $NiCl_2(Ph_3P)_2(dmso)_2$ has the same spin de-

generacy as that of $Ni(dmso)_6^{2+}$ and their MCD spectra are similar to each other, the MCD spectrum of $NiCl_2(Ph_3P)_2(dmso)_2$ may arise from the MCD C-term.

It has been shown that the major contribution to the MCD of charge-transfer bands of tetrahalogenonickel(II) complexes comes from the C-term, because of the variation of the MCD spectrum with temperature.[15] The analysis of the MCD spectra of the paramagnetic tetrahedral complex $NiCl_2(Ph_3P)_2$ was done for the following two cases. *Case A)* The energy levels are calculated by the above approximation. The calculated energy levels are shown in Fig. 10 as C_{2v}+S.O. *Case B)* The ligand field is assumed to be rigorously tetrahedral and the effect of spin-orbit coupling is included. The magnitude of ligand field parameter D_q is assumed to be 450 cm^{-1}, which is a simple numerical average of the D_q's of $NiCl_4^{2-}$ and $Ni(Ph_3P)_4^{2+}$. The calculated energy levels are shown in Fig. 10 as T_d+S.O.

By using the eigen-functions in *case B)*, we have calculated the levels of MCD parameters A and C for all the allowed transitions among the levels split by spin-orbit interaction in the $^3T_1(F)\rightarrow{}^3T_1(P)$ absorption band; the results are given in Table 1. In the calculation of the MCD parameter B the mixing of the charge transfer states will be significant, but it is hard to evaluate it correctly. Therefore we neglected B. The calculated value of A for the transition $A_1\rightarrow T_2$ is negative, and it leads to a positive dispersion of the MCD spectrum. We shall use the dipole strength D defined in Ref. 9. The calculated value of A/D for the transition $A_1\rightarrow T_2$ is in good agreement with the experimental value -8.4β, which is obtained by assuming that the MCD of 0.01 M solution of $NiCl_2(Ph_3P)_2$ in CH_3CN in the range 14000—18000 cm^{-1} is dominated by the A-term. The magnitudes of the A- and C-terms are dependent, furthermore, on the frequency (ν), the width at half-maximum height of the absorption line (Γ), and temperature (T).[8,9] If we assume $\Gamma h/2\pi\approx 4000$ cm^{-1} and $kT\approx 200$ cm^{-1}, where h is Planck's constant and k is the Boltzmann constant, the A-term for the transition $A_1\rightarrow T_2$ is almost the same order of magnitude as the C-term for the transitions $T_1\rightarrow T_1$, E, and T_2. The A-term is dominant for the transition $A_1\rightarrow T_2$ and the C-term is dominant for the transitions $T_1\rightarrow T_1$, E, and T_2. The C-terms of the latter compose a positive dispersion of the MCD spectrum. Therefore, a positive dispersion of the observed MCD spectrum can be interpreted as the overlap of line shapes due to the A-term of the transition $A_1\rightarrow T_2$ and the C-terms of the transitions $T_1\rightarrow T_1$, E, and T_2.

Table 1. Calculated values of MCD and absorption parameters[a] for the transitions from each level split from $^3T_1(F)$ to each level split from $^3T_1(P)$

Transition	Excitation energy (cm^{-1})	A[b]	C[b]	D[c]	A/D
$A_1\rightarrow T_2$	16400	−79.4	0	95.3	-8.3β
$T_1\rightarrow T_1$	16380	−6.3	3.0	7.2	-8.8β
$\rightarrow E$	16150	−0.5	1.1	2.5	-0.2β
$\rightarrow T_2$	16010	−0.7	−2.7	6.4	-1.1β
$E\rightarrow T_1$	15690	0.3	0.0	0.8	0.4β
$\rightarrow T_2$	15320	0.0	0.0	0.0	0.0
$T_2\rightarrow A_1$	15690	0.0	0.0	0.1	0.0
$\rightarrow T_1$	15460	0.0	0.0	0.0	0.0
$\rightarrow E$	15230	0.0	0.0	0.0	0.0
$\rightarrow T_2$	15090	0.0	0.0	0.0	0.0

a) All values of parameters A, C, and D include the Boltzmann distribution factor of the initial state at room temperature. b) In units of $10^4\beta p^2$, where β is the Bohr magneton and $p=\langle t_2\|er\|e\rangle$. c) In units of 10^3p^2.

In *case A)*, the effects of lower symmetry field and the spin-orbit coupling are comparable. Both the spin and the orbital degeneracies are removed. However, since the eigen-functions are not real, the MCD parameters A, B, and C are nonzero. We have estimated the B-term with the following approximation. As the states to be mixed into one of the states split from $^3T_1(F)$ by the external magnetic field, we have considered only the rest of the states split from $^3T_1(F)$. In the same way, we have considered only the rest of the split states as the states to be mixed into one of the states split from $^3T_1(P)$. By using the eigen-functions in *case A)*, we have calculated the values of MCD parameters A, B, and C. Contrary to our expectation, all of these parameters are found to be smaller than about 1% of the values obtained in *case B)*. Therefore, in this case we cannot explain the observed magnitude of $[\theta]_M$. The main cause of such small valuse seems to be the fact that we estimated the effect of the lower symmetry field and the spin-orbit coupling to be of the same order of magnitude. In fact, the effective field operating in $NiCl_2(Ph_3P)_2$ in solution might be very close to that of tetrahedral symmetry. More extensive study would be necessary with respect to this point.

Proton Nuclear Magnetic Resonance Studies. Proton NMR spectra of dihalogenobis(tertiary phosphine)-nickel(II) complexes have been investigated extensively.[21-26] The signals of the phenyl ring protons of the paramagnetic tetrahedral species are usually substantially displaced from the resonance positions of the diamagnetic species. The shift is upfield for the ortho and para protons and downfield for meta protons; it is interpreted as arising from a contact interaction with unpaired electrons which have been partially delocalized from a nickel atom to the π-orbital of the ligand.[21,22] The kinetics of ligand exchange in the tetrahedral complexes and the thermodynamics and kinetics of the diamagnetic planar↔paramagnetic tetrahedral interconversion have been studied,[23-26] but these studies were done only on the solutions in inert solvents. As we have shown in the studies of the MCD and absorption spectra, the complex $NiCl_2(Ph_3P)_2$ in coordinating solvents can be in equilibrium between a paramagnetic tetrahedral form and a paramagnetic octahedral form.

The proton NMR spectra of $NiCl_2(Ph_3P)_2$ in DMSO at various concentrations are shown in Fig. 11. As the concentration increases, the splitting of the ortho,

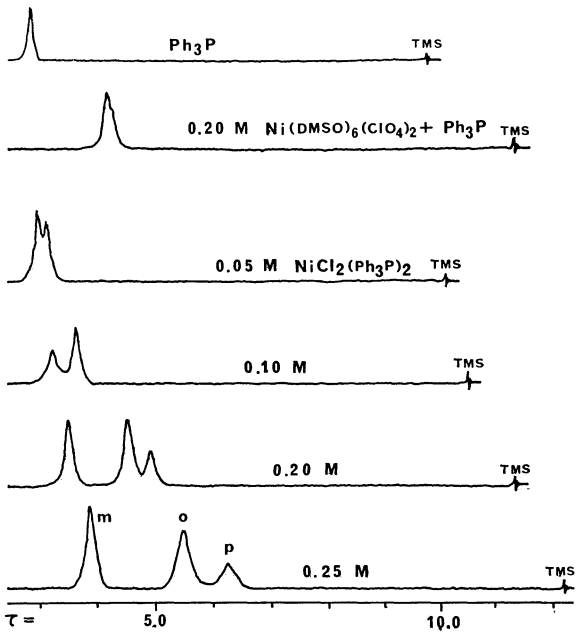

Fig. 11. Proton NMR spectra at several concentrations of the solution of $NiCl_2(Ph_3P)_2$ in DMSO at room temperature. Proton shifts are shown relative to the protons of tetramethylsilane (TMS) in CCl_4 ($\tau=10.0$) as an external standard. The signal of TMS as an internal standard shifts depending on the concentration of nickel(II) ions, and the position is shown as TMS in each spectrum. The spectrum of triphenylphosphine which is added to 0.20 M solution of $Ni(dmso)_6(ClO_4)_2$ in DMSO and the spectrum of triphenylphosphine dissolved in DMSO are shown for comparison.

meta and para protons increases and the signals of phenyl ring protons generally shift upfield. When some excess Ph_3P is added to the 0.2 M solution of $NiCl_2(Ph_3P)_2$, the splitting of the phenyl ring protons decreases and all the signals approach the resonance position of the Ph_3P which is added to the 0.2 M solution of $Ni(dmso)_6(ClO_4)_2$ in DMSO. The signal of the TMS added to a 0.2 M solution of $Ni(dmso)_6(ClO_4)_2$ in DMSO and that of Ph_3P added to the same solution both shifted by 1.5 ppm from the respective signals in the absence of the nickel complex. The signal of TMS in 0.2 M solution of $NiCl_2(Ph_3P)_2$ in DMSO also shifted by the same magnitude. Thus there are nearly the same amount of paramagnetic nickel(II) ions in both 0.2 M $NiCl_2(Ph_3P)_2$ in DMSO and 0.2 M $Ni(dmso)_6(ClO_4)_2$ in DMSO. With respect to the signal of non-coordinating Ph_3P, the ortho and para protons are shifted upfield and the meta protons are shifted downfield. The characteristic shifts are interpreted as arising from the contact shift originating in the paramagnetic tetrahedral form. The configurational equilibrium is significantly dependent on the concentration, and the increase of concentration is favorable for the tetrahedral form in DMSO. The rate of ligand exchange or structual interconversion is fast, since no new peaks and only averaged resonances are observed, showing that it is faster than 10^2 s^{-1}. The splitting of the phenyl ring protons decreases

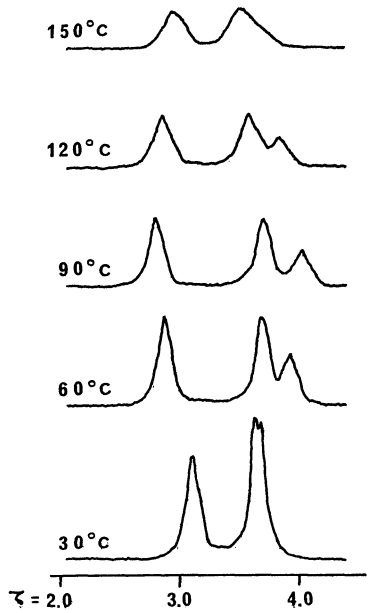

Fig. 12. Proton NMR spectra of 0.1 M solution of $NiCl_2(Ph_3P)_2$ in DMSO in the temperature range 30 to 150 °C.

gradually, within the time scale shown in Fig. 6, and the signals approach the position of the non-coordinating Ph_3P.

The proton NMR spectrum of 0.1 M solution of $NiCl_2(Ph_3P)_2$ in DMSO in the temperature range 30 to 150 °C is shown in Fig. 12. An increase of the contact shift, which reveals the increase of the paramagnetic tetrahedral complex, is observed as the temperature is raised up to 90 °C. As the temperature is raised further, the contact shift begins to decrease and the line broadening is observed. The temperature dependent behaviour may be interpreted as showing that the solvated octahedral molecule $NiCl_2(Ph_3P)_2(dmso)_2$ tends to become tetrahedral $NiCl_2(Ph_3P)_2$ by expelling the coordinated solvent as the temperature is raised; then the rate of ligand exchange increases and the effect becomes predominant at temperatures higher than 100 °C. However, such a change of the proton NMR spectrum is not observed in the

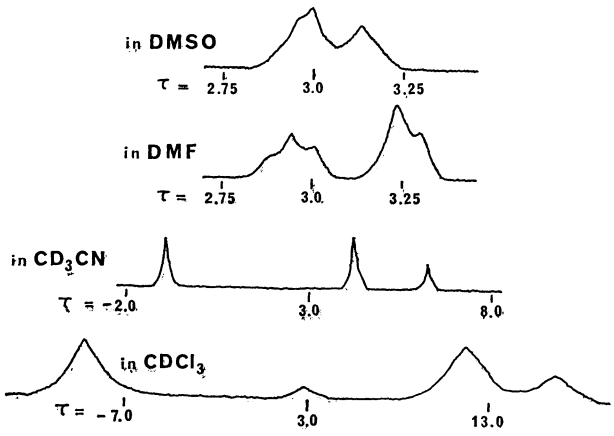

Fig. 13. Proton NMR spectra of $NiCl_2(Ph_3P)_2$ in various solvents at the same concentration; 0.05 M.

solutions in either CH_3CN or $CHCl_3$. The contact shift increases as the temperature is cooled down to -50 °C in both CH_3CN and $CHCl_3$.

The proton NMR spectra of $NiCl_2(Ph_3P)_2$ in various solvents at the same concentration, 0.05 M, are shown in Fig. 13. The ratio of the paramagnetic tetrahedral form of $NiCl_2(Ph_3P)_2$ increases in the solutions in the order DMSO<DMF<CH_3CN<$CHCl_3$. When excess Ph_3P is added to these solutions, all the signals are found to approach the position of the signal of non-coordinating Ph_3P. Therefore the rate of ligand exchange of Ph_3P is faster than 10^2 s^{-1} in all these solutions. It should therefore be noted that the weak signal at about $\tau=3$ in $CDCl_3$ solution is not a signal of the non-coordinating Ph_3P.

Conclusions

The MCD, absorption, and proton NMR spectra thus exhibit consistently the structural interconversions of $NiCl_2(Ph_3P)_2$ in various solvents. Generally, the paramagnetic tetrahedral form of this compound is more stable at high concentrations in both coordinating and non-coordinating solvents. In coordinating solvents, such as DMSO and DMF, the solvent-coordinated paramagnetic octahedral species $NiCl_2(Ph_3P)_2$(solvent molecule)$_2$ are found to increase as the concentration of $NiCl_2(Ph_3P)_2$ is decreased and also as time goes on after making the solution. Further, it is found that the coordinated Ph_3P tends to leave gradually and the solvated complex $NiCl_2$(solvent molecule)$_4$ is formed. However, these solvent molecules will not be so strongly coordinative in comparison with Ph_3P, since it is found that the ratio of the paramagnetic tetrahedral species $NiCl_2(Ph_3P)_2$ increases as the temperature of the solution containing the solvated species is raised.

In non-coordinating solvent $CHCl_3$, no solvated octahedral compound is observed. Configurational isomers of a paramagnetic tetrahedral and a diamagnetic square-planar $NiCl_2(Ph_3P)_2$ are observed. The molecule of the former isomer will retain the distorted tetrahedral configuration which it has in the crystal. The magnitude of the proton NMR signal at $\tau=3$ grows gradually and coincidently all the other signals, which are due to the paramagnetic tetrahedral species, are reduced in intensity without changing their positions. At the same time, the absorption spectra of the solution change to show the bands only in the energy region higher than 25000 cm^{-1}; these bands have a strong resemblance to those of $Ni(SCN)_2(Ph_3P)_2$ (Fig. 4) and may be identified as those of a diamagnetic square-planar species. The rate of interconversion between the paramagnetic tetrahedral form and the diamagnetic square-planar form is sufficiently slow on the NMR time scale, *i.e.* less than 10^2 s^{-1}. It seems to be almost one-way from the paramagnetic tetrahedral form to the diamagnetic square-planar form and irreversible. As the former form decreases gradually, a yellow precipitate is observed to grow. The ratio of the former form to the latter one is greater at high concentrations, and the yellow precipitate grows faster at low concentrations. When the filtrate of the yellow precipitate is dried, only Ph_3P remained. We identified this yellow precipitate to be $NiCl_2$ by measuring the magnetic susceptibility and the melting point. It appears therefore that the paramagnetic tetrahedral $NiCl_2(Ph_3P)_2$ decomposes gradually to $NiCl_2$ and $2Ph_3P$, and since the solvent does not coordinate, $NiCl_2$ precipitates as Ph_3P leaves.

The paramagnetic octahedral species, the paramagnetic tetrahedral species, and the diamagnetic square-planar species seem to coexist in the solution of $NiCl_2(Ph_3P)_2$ in CH_3CN. Some nickel(II)–acetonitrile complexes, $Ni(CH_3CN)_6(BF_4)_2$, $NiCl_2(CH_3CN)_4$, and $NiCl_2(CH_3CN)_2$, have been reported. A chloride ion is well known to be a stronger coordinating ligand than CH_3CN.[27] The MCD and absorption spectra show that the proportion of the diamagnetic species is smaller in the solution in CH_3CN than in $CHCl_3$. The proton NMR spectra show a greater contact shift in $CHCl_3$ than in CH_3CN. This will be due to the liability of ligand exchange between Ph_3P and CH_3CN. Most of the absorption in the range 14000 to 19000 cm^{-1} in Fig. 7 will be due to the tetrahedral $NiCl_2(Ph_3P)_2$, since the tetrahedral complex $NiCl_2(CH_3CN)_2$ will show an absorption band with the peak at about 13000 cm^{-1}. As the time goes on after dissolving $NiCl_2(Ph_3P)_2$ in CH_3CN, a pale yellow precipitate is observed to grow, but it is not so much as in the solution in $CHCl_3$ and the proton NMR signal at about $\tau=3$ is found to grow gradually. The absorption spectrum does not change drastically as in the case of $CHCl_3$ solution; it changes only slightly, suggesting the coexistence of a small amount of a tetrahedral $NiCl_2(CH_3CN)_2$ and an octahedral $NiCl_2(CH_3CN)_4$.

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